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ARTICLE

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Deciphering the Origin of Million-fold Reactivity Observed for the Open Core Diiron $[HO\text{-}Fe^{III}\text{-}O\text{-}Fe^{IV}{=}O]^{2+}$ Species Towards C-H Bond Activation: Role of Spin-states, Spin-coupling, and Spin-cooperation

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High-valent metal-oxo species have been characterised as key intermediates in both heme and non-heme enzymes that are found to perform efficient aliphatic hydroxylation, epoxidation, halogenation, and dehydrogenation reactions. Several biomimetic model complexes have been synthesised over the years to mimic both the structure and function of the metalloenzymes. The diamond-core $[Fe_2(\mu\text{-}O)_2]$ is one of the celebrated models in this context as this has been proposed as the catalytically active species in soluble methane monooxygenase enzyme (sMMO) which perform the challenging chemical conversion of methane to methanol at ease. In this context, report of an open core $[(HO(L)Fe^{III}\text{–}O\text{–}Fe^{IV}(O)(L)]^{2+}$ (**1**) gains attention as this activates C-H bonds a million-fold faster compared to the diamond-core structure and has the dual catalytic ability to perform hydroxylation as well as desaturation with organic substrates. In this study, we have employed density functional methods to probe the origin of the very high reactivity observed for this complex and also to shed light on how this complex performs efficient hydroxylation and desaturation of alkanes. By modelling fifteen possible spin-state for **1** that could potentially participate in the reaction mechanism, our calculations reveal a doublet ground state for **1** arising from antiferromagnetic coupling between quartet Fe^{IV} centre and sextet Fe^{III} centre regulate the reactivity of this species. The unusual stabilisation of high-spin ground state for $Fe^{IV}{=}O$ is due strong overlap of $Fe^{IV}\sigma^*_{z^2}$ with $Fe^{III}\pi^*_{xz}$ orbital, reducing the antibonding interactions via spin-cooperation. The electronic structure features computed for **1** is consistent with experiments offering confidence on the methodology chosen. Further, we have probed various mechanistic pathways for the C-H bond activation as well as –OH rebound/desaturation of alkane. An extremely small barrier height computed for the first hydrogen atom abstraction by the terminal $Fe^{IV}{=}O$ unit found to be responsible for the million-fold activation observed in the experiments. The barrier height computed for –OH rebound by the Fe^{III}-OH unit is also smaller suggesting a facile hydroxylation of organic substrates by **1**. A strong spin-cooperation between the two iron centres also reduces the barrier for second hydrogen atom abstraction, thus making the desaturation pathway competitive. Both the spin-state as well as spin-coupling between the two metal centres are playing a crucial role in dictating the reactivity for species **1**. By exploring various mechanistic pathways, our study unveils the fact that the bridged μ-oxo group is poor electrophile for both C-H activation as well for –OH rebound. As more and more evidence is gathered in recent years for the open core geometry of sMMO enzymes, the idea of enhancing the reactivity via an open-core motif has far-reaching consequences.

Introduction

High-valent metal-oxo complexes are of great interest due to their potent catalytic abilities.[1-25] Dinuclear metal-oxo complexes have different types of the metal centre, but iron is the most common metal centre to oxidise C-H bonds by dioxygen activation mechanism, in which high-valent oxo-iron species are often postulated and demonstrated to act as the actual oxidising species.[26-33] Membrane-bound methane monooxygenase (MMOs) containing copper are known,[34-37] but the longest known MMOs are soluble proteins containing a dinuclear iron active site.[27, 38-40] High-valent intermediate Q of soluble methane monooxygenase (sMMO) is a two-electron oxidant that effects the hydroxylation of methane.[41-47] For these reasons, complexes based on high-valent iron have been proved as a compelling tool in the activation of inert C−H bonds, both in biochemical and synthetic oxidation processes.[48-50]

The active site structure of the sMMO possesses a $[Fe^{IV}_2(\mu\text{-}O_2)]$ diamond core motif,[45, 51-56] and this unit is known to be responsible for activation of inert C-H bonds such as those of methane.[57] This has inspired several groups to utilise both heme,[50, 58-60] and non-heme[61] ligand framework to synthesise biomimetic models, which are both structural and functional mimic of the enzyme.[62] Among various reported diiron enzymes that possess diiron(IV) at the active centre, two classes of enzymes clearly emerge with enzymes such as sMMO or ToMO performing hydroxylation of aliphatic and aromatic substrates while enzymes such as Δ9 desaturase (Δ9D)[63-65] perform

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Improved Adhesion and Corrosion Resistant Performance of Polyurethane Coatings on Anodized Mg Alloy for Aerospace Applications

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In the current investigation, we targeted to improve the adhesion and corrosion resistant behavior of AZ31 Mg alloy by executing the two-stage treatment; initially by anodization then followed by the deposition of polyurethane (PU) coatings. The impact of the different anodized layers on the adhesion and corrosion protective performance of PU-coated AZ31 Mg substrates was systematically estimated by various characterization techniques. Surface characterization results revealed the influence of silicate content in the anodization bath on the surface microstructure of anodized layers. Surface wettability of Mg substrates after anodization was significantly improved (nearly 25°), confirming the enhanced surface hydrophilicity, possibly due to the higher surface roughness. From the scratch test results, the PU/A75Si coating exhibited the highest adhesion strength with a critical load of 4.8 ± 0.3, which corresponds to about ten-fold of improvement in comparison to PU/Bare. Corrosion test results confirmed the enhanced corrosion protection behavior of PU/A75Si coatings with higher values of R_{ct} ($8.72 \times 10^7\,\Omega\,cm^2$), and R_f ($1.881 \times 10^7\,\Omega\,cm^2$) with the lowest values of i_{corr} (2.0120×10^{-10} Acm^{-2}) compared to that of PU/Bare samples. Based on the attained outcomes, it was concluded that the anodized layer could increase the adhesion between the polyurethane coatings and base substrate, which is the necessary factor in enhancing the corrosion resistant behavior of polyurethane coatings on AZ31 Mg substrates.

Keywords AZ31 Mg alloy, adhesion strength, corrosion, EIS, polyurethane coating

1. Introduction

Magnesium (Mg) alloys have been broadly employed in aerospace, automobile, defense, and biomedical devices owing to their high stiffness and specific strength, superior machinability, and castability (Ref 1-3). Predominantly, weight reduction by the practice of low-density Mg alloys could save fuel consumption and decreases harmful gas emissions. The main restriction to the utilization of Mg alloys as a structural material is their low corrosion resistance because of their high chemical reactivity of Mg (Ref 4, 5). Hence, an enhancement in corrosion resistant behavior of Mg alloys is of vital prominence and highly desirable prior to their large-scale applications.

One of the most efficient strategies to mitigate corrosion on Mg alloys is to isolate the Mg surface from the aggressive environment by forming a coating layer over the Mg surface (Ref 6, 7). In general, coatings on Mg alloys could be categorized as deposited coatings and conversion coatings. Deposited coatings are comprised of polymeric, metallic, inorganic, and organic coatings, respectively (Ref 8, 9). Formation of conversion coating occurs by the multifaceted interaction of metal dissolution and precipitation, which comprise chemical conversion coatings, anodization, fluoride and alkaline treatments, and silanization (Ref 10, 11). Many researchers have dedicated their efforts in assessing the corrosion protection performance of coated Mg substrates in various harsh environments (Ref 12-14).

Polyurethane (PU) is one of the widely used organic coatings in multipurpose applications. PU usually consists of urethane and urea groups, which can be obtained by reacting mainly polyol, isocyanate, and diamine. The PU coating has high adhesive strength, and anticorrosion properties into metal surface (Ref 15, 16). The PU coating has a good ability to block/reduce the substrate erosion induced by oxygen, water, as well as the corrosive ions (Ref 17, 18). The protective properties tuned by choosing the monomers and their contents. Various siloxane and fluro-based monomers also used to improve the protective properties in marine environments. Although PU coatings have been commercially employed for several decades, the adhesion on the metallic materials is still being enhanced to prolong the performance of PU coatings. In general, adhesion strength is intensely influenced by the chemical interactions between the substrate and polymeric coating, which is further enhanced by adopting appropriate surface pretreatments.

Many research works have been committed to evaluating the exact relation between organic coatings and the pretreated metallic surface in terms of its surface characteristics such as

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4-(2,3-Dichlorophenyl)piperazin-1-ium picrate

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Keywords: 1-(2,3-dichlorophenyl)piperazinium picrate; crystal structure; supramolecular interaction.

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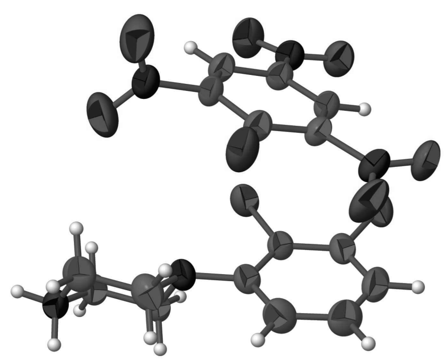
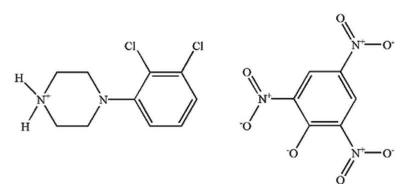
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_6H_2N_3O_7^-\cdot C_{10}H_{13}Cl_2N_2^+$, crystallizes with one 1-(2,3-dichloro-phenyl)piperazine (DP) cation and one picrate (PA) anion in the asymmetric unit. In the crystal structure, the DP cation and PA anion are interconnected *via* several N—H···O and C—H···O hydrogen bonds. The DP cation and PA anion are further connected through C—Cl···π [3.8201 (4), 3.7785 (4) Å] and N—O···π [3.7814 (4) Å] interactions. The DP cations are further interconnected *via* a weak intermolecular Cl···Cl [3.2613 (4) Å] halogen–halogen interaction. The combination of these supramolecular interactions leads to a herringbone like supramolecular architecture.

3D view



Chemical scheme



Structure description

1-(2,3-Dichlorophenyl)piperazine (DP), a precursor in the synthesis of potent drugs such as aripiperazole (AP) (Oshiro *et al.*, 1998), is used as an antipsychotic drug for the treatment of schizophrenia (Braun *et al.*, 2009; Frank *et al.*, 2007). A survey of the Cambridge Structural Database (CSD version 5.40, updates of May 2019; Groom *et al.*, 2016) shows that there are no reports of salt and co-crystal forms of this compound. We herein report the crystal structure of a new solid form of DP, 1-(2,3-dichloro-phenyl)-piperazinium picrate (**1**).

The title salt, **1**, crystallizes in the monoclinic $P2_1/n$ space group. The asymmetric unit contains one (DP) cation and one picrate (PA) anion as shown in Fig. 1. In **1**, the pyrazine ring of the cation molecule adopts a chair conformation with N—H and C—H bonds in axial–axial and equatorial–equatorial positions (Singh *et al.*, 2015; Maia *et al.*, 2012).

The protonated DP cation interacts with the neighbouring deprotonated PA anions *via* N1—H1*A*···O4^{i}, N1—H1*B*···O2^{ii} and N1—H1*B*···O7^{ii} hydrogen bonds and C2—